

Covalently attached sandwich structure from colloidal particles and diazo-resin

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Abstract

A covalently attached sandwich structure between layers and particles has been fabricated from –COOH-containing copolymer latex particles and $-N_2^+$ -containing polymers by self-assembly combined with a UV irradiation technique. The ionic bonds involving the layers and particles change to covalent bonds under UV irradiation and the sandwich structure become very stable toward polar organic solvents and electrolyte aqueous solutions.

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1. Introduction

Self-assembly of oppositely charged polyelectrolytes via electrostatic attraction was first reported in 1991 [1,2] by Decher and Hong and has been developed rapidly [3–5]. The main defect of the multilayer films from electrostatic force is less stability toward polar solvents or electrolyte aqueous solutions. In recent years a kind of stable self-assembly film was successfully fabricated using $-N_2^+$ -containing polymers as photosensitive polycations [6–8]. The ionic linkage involved in the multilayers will convert to covalent bonds with exposure of the $-N_2^+$ -containing films to UV light [9–11]. Self-assembly using colloidal particles as a component has attracted more and more attention recently [12–14]. Ordered arrays from colloidal particles represent an important and interesting topic relating to colloidal and optical crystals [15–17]. Numerous of macroporous materials from various components including inorganic, organic, metallic, and ceramic substances have been successfully made with colloidal crystals as templates [18–21]. It is expected that optical crystals will play a strategic role in the development of photonic techniques associated with the communication and computer areas [22,23]. In nature the opal was believed to be formed from ordered arrays of SiO_2 sediment followed by the infiltration of water-soluble silicate [24]. It is a real

challenge to make ordered array materials according to the mode of opal formation in nature. In this article we present a method to prepare a stable sandwich structure from –COOH-attached colloid particles and an $-N_2^+$ -containing polymer. It may be interest for the synthesis of stable sandwich structure comprising ultrathin film and particles including inorganic clusters.

2. Experimental

2.1. Materials and instruments

A carboxyl-attached colloidal particle of P(St/BA/AA) was synthesized according to the method in [25] with some modifications: 80 ml of aqueous solution (A) containing $K_2S_2O_8$ (0.8 g), Na_2CO_3 (0.3 g), sodium dodecyl sulfate (SDS) (1.2 g), OP-10 (0.2 g) (OP-10: $C_9H_{20}C_6H_4(OC_2H_4)_{10}OH$) and 35 ml of solution (B) consisting of styrene (St)/butyl acrylate (BA)/acrylic acid (AA) (90:5:5 v/v/v) were added into the funnels and then dropped into a 250-ml three-necked bottle in 3 h under stirring at $\sim 78^\circ C$ to obtain a milky product. St, AA, and BA were distilled before use; all other chemicals were of analytical grade. The atomic force microscopy (AFM) images of the colloidal particles were obtained on a Nanoscopy IIIA (Digital Instruments, Inc.) in a tapping mode. Commercial silicon probes (Model

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TESP-100) with a typical resonant frequency around 300 kHz were used to obtain the images.

Diazo-resin (DR) was synthesized in a three-necked bottle, to which 3.61 g (10 mmol) of diphenylamine 4-diazonium chloride and 30 ml of concentrated sulfuric acid were added under stirring at $\sim 0^\circ\text{C}$. The HCl generated in the reaction was removed by a water pump. Next 0.30 g (10 mmol formaldehyde) of paraformaldehyde, which was carefully powdered already, was added batchwise to the bottle. The mixture was stirred at $0\text{--}5^\circ\text{C}$ for 3 h and then was poured into 100 ml of ice water and filtered. Into the filtrate, 10 g of ZnCl_2 in 15 ml water was added, and the diazo-resin (1/2 ZnCl_2 complex salt) as a green yellow powder was precipitated and then was washed alternately with saturated ZnCl_2 aqueous solution and ethanol for three times and filtered and dried under vacuum in the dark; 2.78 g (77%) DR was obtained with a M_n about 2500 g mol^{-1} . UV-vis spectra were recorded on a Shimadzu UV-250 spectrophotometer.

2.2. Preparation of the sandwich film

A quartz wafer ($10 \times 30 \times 2\text{ mm}$) pretreated at 70°C in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (7:3 v/v) mixture for 30 min to create a clean and hydrophilic surface, or a piece of freshly cleaved mica ($10 \times 30 \times \sim 0.2\text{ mm}$), was used as the substrate. It was dipped in DR aqueous solution (2 mg in 1 ml H_2O) for 5 min, rinsed with water three times, air-dried, and then immersed in a diluted aqueous emulsion (the original latex was diluted to 1000 times by water) for 5 min, followed by exposure to UV light (80-W medium-pressure mercury lamp at a distance of 10 cm for 2 min), rinsed with water three times, and air-dried to complete an assembly cycle. In each cycle a DR-colloidal particle layer was fabricated on both sides of the substrate. The assembly cycle was repeated until the desired sandwich structure was achieved. The assembly process can be monitored spectrometrically by determining the absorbance of the films at 200–250 nm (the absorption of phenyl moiety). All the processes were carried out in the dark.

3. Results and discussion

The morphology of the copolymer latex particles visualized by TEM is shown in Fig. 1. We can see that the average diameter of the particles is $\sim 90\text{ nm}$ and the particles are not strictly monodispersed.

Figure 2 shows the UV-vis spectra of the sandwich structure in the different assembly cycles. We can see that the absorption bands at ~ 200 and $\sim 250\text{ nm}$, which are characteristic absorptions of the phenyl unit, increase linearly with the number of assembly cycles (inset plot). This indicates that the layer-by-layer assembly from colloidal particles and diazo-resin proceeds regularly.

In fact, some of SDS, OP-10, and Na_2CO_3 have existed in the diluted latex, which was used for assembly in the present

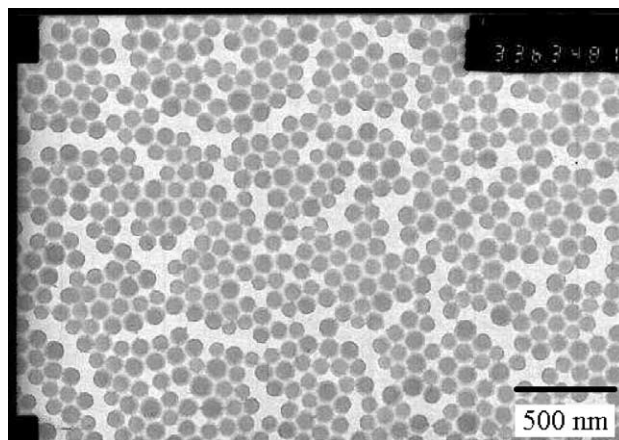


Fig. 1. The TEM image of the P(St/BA/AA) latex particles.

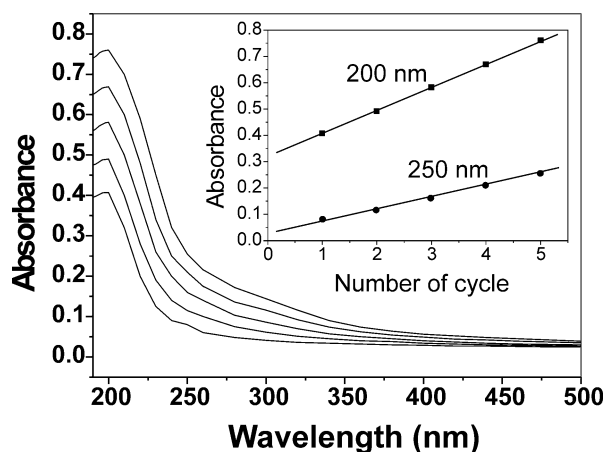


Fig. 2. The UV-vis spectra of the assembly from the latex particles (salts and surfactants were not removed) and DR. The inset plot shows that the absorbance of the films at 200 and 250 nm changes linearly with the number of assembly cycles.

research work. To confirm the effect of these on the assembly, we separated the colloidal particles from the latex by centrifugation, added the same amount of water to wash the particles, and repeated the centrifugation and washing three times. We obtained a purified colloidal particle water dispersion instead of the diluted latex to be assembled with DR, the results obtained are shown in Fig. 3. As compared with Fig. 2, we can see that either the latex or the water dispersion of purified colloidal particles was used in assembly; the absorbance of the assembled films changes almost in same manner. This means that the effect of the trace salts or surfactants on the assembly of the colloidal particles is very limited. In present experiment the concentrations of the SDS ($< 0.012\text{ g l}^{-1}$), OP-10 ($< 0.002\text{ g l}^{-1}$), and Na_2CO_3 ($\leq 0.003\text{ g l}^{-1}$) in the diluted latex used for assembly are very low, so their effect could be ignored.

Figure 4 shows the AFM image of the sandwich from two assembly cycles. We can see that the colloidal particles involving in the sandwich can be visualized clearly. The circles represent the particles, among them those with bright circles

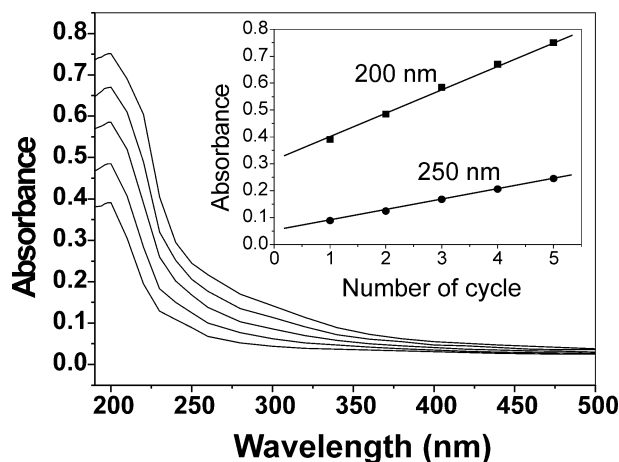


Fig. 3. The UV-vis spectra of the assembly from the purified particles (salts and surfactants were removed by centrifugation) and DR. The inset plot shows that the absorbance of the films at 200 and 250 nm changes linearly with the number of assembly cycles.

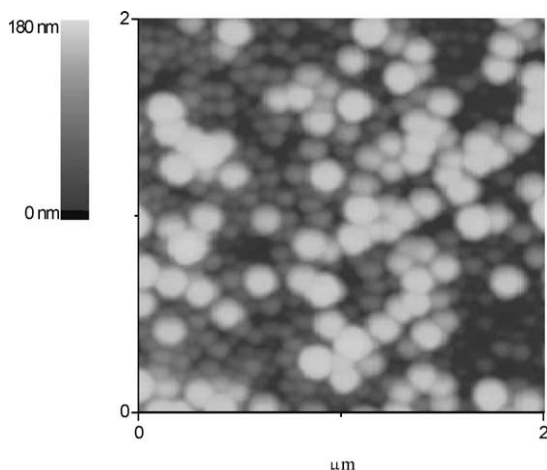


Fig. 4. The AFM image of a two-cycle sandwich fabricated with UV irradiation in each cycle from colloidal particles and DR on mica.

represent the particles in the surface layer of the structure, and the shaded ones represent those in the bottom layer.

The thickness of the DR layer in the assembly film is around 1.5–2.0 nm [26], but the diameter of the colloidal particles is about 90 nm, larger than the layer thickness, so the particles usually are difficult to attach to the layers if no photoreaction occurs in the sandwich. In order to verify this result further, the assembly between poly(*N*, *N*-diallyl-*N*, *N*-dimethylammonium chloride) (PDDAC) as polycation and the –COOH-containing colloidal particles was performed under the same conditions. As shown in Fig. 5, few particles were found in the PDDAC layer. Therefore it is believed that photoreaction plays a key role in forming sandwich structures in the assembly of DR with colloidal particles.

The photoreaction taking place in the sandwich can be schematically illustrated as in Scheme 1. After UV irradiation the sandwich structure become very stable toward polar solvents or electrolyte aqueous solutions because the nature

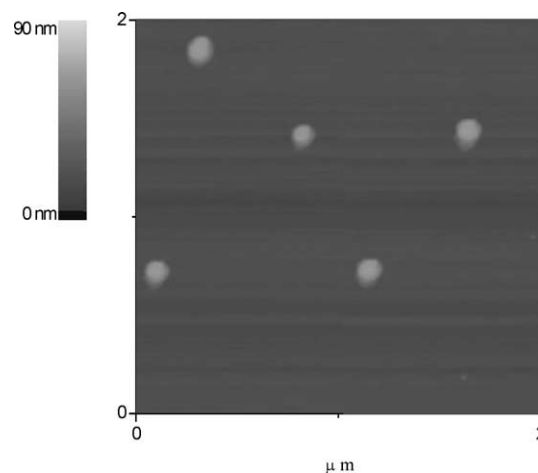


Fig. 5. The AFM image of a four-cycle film fabricated from colloidal particles and PDDAC on mica.

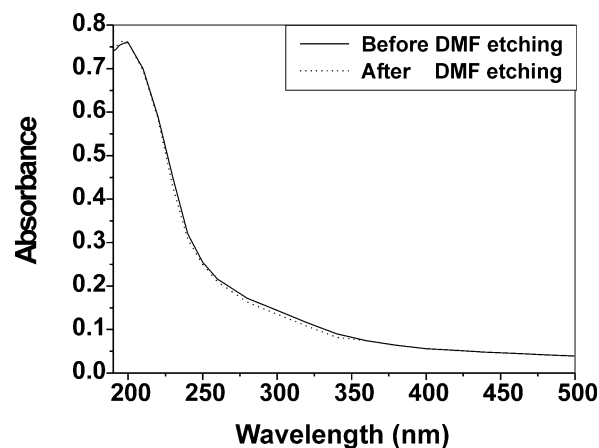
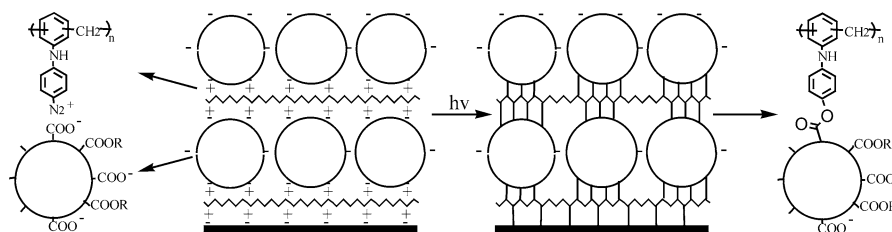


Fig. 6. The UV-vis spectra of the stable sandwich (fabricated with UV irradiation) before (solid line) and after (dot line) etching with DMF at $\sim 25^\circ\text{C}$ for 24 h.

of the bond between the layer and the particles has changed from ionic to covalent. Figure 6 shows the UV-vis spectrum (the dotted line) of the sandwich from five cycle assemblies combining the photoreactions in each cycle, etched by DMF for 24 h ($\sim 25^\circ\text{C}$). As compared with the original one (the solid line), almost no changes were found in the spectrum. It means that the sandwich fabricated described above is very stable toward polar solvents. The same results were obtained as the sandwich mentioned was dipped in a 1 M NaCl aqueous solution.

The photoreactions taking place in assembly layers play a key role in achieving a stable sandwich structure from DR and latex particles, because the structure constructed without UV irradiation in each assembly cycle is not stable to the etching of DMF or electrolyte aqueous solutions. Figure 7 shows the UV-vis spectra of a five-cycle film from DR and colloidal particles, which was fabricated under no exposure to UV light in each assembly cycle; with etching for 24 h ($\sim 25^\circ\text{C}$, in the dark) in DMF, the absorbance of the film decreases greatly (dotted line) as compared with that of



Scheme 1. Schematic illustration of the photoreaction taking place in the sandwich.

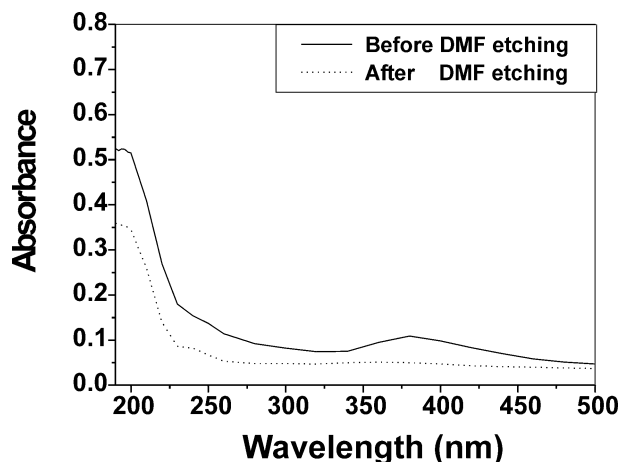


Fig. 7. The UV-vis spectra of the unstable film (fabricated without combining UV irradiation) before (solid line) and after (dotted line) etching with DMF at $\sim 25^\circ\text{C}$ for 24 h.

the original one (solid line). This means that the assembly structure without photoreaction is unstable toward the DMF etching.

4. Conclusions

A stable sandwich structure has been prepared from carboxy-containing particles and diazo resin by self-assembly combined with a UV radiation technique. The photoreaction taking place between the layers of the film has been confirmed to play a key role in the stability of this kind of film toward polar solvents or electrolyte aqueous solutions, because stable sandwiches were not formed without UV irradiation in each fabrication cycle. The particles involved in a sandwich structure have been visualized clearly by atomic force microscopy. It was believed that the ionic linkages between the layers and particles convert to covalent bonds under UV radiation. The covalently attached sandwich structures are very stable against etching from polar organic solvents or electrolyte aqueous solutions.

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